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NANO ENABLED THERMO-MECHANICAL MATERIALS IN ADHESIVE JOINTS: A NEW PARADIGM TO MATERIALS FUNCTIONALITY (PREPRINT)

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14. ABSTRACT
One of the barriers in achieving adequate through-thickness thermal conductivity in composite materials and also in composite joints is the extremely low thermal conductivity of resins (polymer) or adhesives (typically 0.3 W/mK). In this paper, a material configuration aligning Multi-wall Nanotube (MWNT) in the thickness direction in adhesive joint is studied to enhance through-thickness thermal conductivity. Initial numerical study indicated that the thermal contact of the conductive phase (in this case is the MWNT) with the adherent surfaces is essential to achieve the desirable through-thickness thermal conductivity in joints. To demonstrate the concept, conductive graphite face sheets were used along with aligned MWNT aligned along the joint thickness. Aligned MWNT infused with resin (adhesive) is processed in joints with plasma etching the surfaces ensuring the ends of the MWNT make thermal contact with the adherent surfaces. The MWNT modified adhesive joint through-thickness thermal conductivity measure to be over 250 W/mK, which exceeded the thermal conductivity of adhesive by several orders of magnitude. Thus, the study demonstrates a new approach as well as opportunities of much needed thermal property tailoring in structural joints.

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Nano enabled thermo-mechanical materials in adhesive joints: a new paradigm to materials functionality

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Abstract

One of the barriers in achieving adequate through-thickness thermal conductivity in composite materials and also in composite joints is the extremely low thermal conductivity of resins (polymer) or adhesives (typically 0.3 W/mK). In this paper a material configuration aligning Multi wall Nanotube (MWNT) in the thickness direction in adhesive joint is studied to enhance through-thickness thermal conductivity. Initial numerical study indicated that the thermal contact of the conductive phase (in this case is the MWNT) with the adherent surfaces is essential to achieve the desirable through-thickness thermal conductivity in joints. To demonstrate the concept, conductive graphite face sheets were used along with aligned MWNT aligned along the joint thickness. Aligned MWNT infused with resin (adhesive) is processed in joints with plasma etching the surfaces ensuring the ends of the MWNT make thermal contact with the adherent surfaces. The MWNT modified adhesive joint through-thickness thermal conductivity measured to be over 250 W/mK, which exceeded the thermal conductivity of adhesive by several order of magnitudes. Thus the study demonstrates a new approach as well as opportunities of much needed thermal property tailoring in structural joints.

Keywords: Through-thickness thermal conductivity, bonded joints, MWNT

1. Introduction

In the quest of reducing life cycle cost and system reliability of aircraft, there is push for developing electric aircraft, reducing or perhaps eliminating rotatory power generation devices. That will require using stationary power devices (such as, rechargeable batteries, capacitors, heat exchangers, etc.) distributed throughout the aircraft. These devices invariably will create hot spots as they are attached to the aircraft structure. Thus, structural systems will require adequate thermal efficiency to efficiently manage the heat generated by these devices. For example, heat generated by a capacitor or battery needs to be taken away to a remote location for other usage. In almost all cases these heat generating devices are attached to the structural members by adhesive joints, thus suitable materials system to enable through-thickness thermal conductivity in adhesive joints.

In current adhesive joints in system design, relatively poor thermal conductivity (K) of adhesives (of ~ 0.3 W/mK) fails to meet the needed K_z at the system level, as structural components are primarily assembled through bonded joints. The approach of mixing carbon nanotubes or nanofibers in adhesive that only improved its thermal conductivity to approximately to 0.7 W/mK [1-3] is not an adequate solution. A through-thickness thermal conductivity (K_z) of adhesive of about 7-10 W/mK will enable efficient multifunctionality

and lean manufacturing of systems to numerous applications, ranging from electronic cooling, efficient space structures, and to dramatically improving the energy conversion and energy harvesting efficiency in thermal structures [4,5].

The thermal transport (conductivity) in solids is controlled by the lattice vibration frequency associated with phonon mean free path, as Ziman [6] and Klemens [7] thoroughly analyzed the phonon characteristics and its mechanism in thermal energy propagation in different solids. The thermal transport at the junction of dissimilar materials, such as in joints, is however influence by phonon scattering at the material interface, which is attributed to the mismatch of the acoustic impedance of the two materials. Cahil et al. [8] in their review paper documented the scientific development of material synthesis and measurement techniques in understanding the physics of thermal transport in nanostructured materials and materials interface at nanoscale devices and attributed the strong dependence of acoustic mismatch on the thermal conduction through the solid-solid interface. Besides, phonon scattering due to acoustic impedance mismatch at the interface, the finite element analysis by Grujicic et al. [9] indicated that surface roughness of the contact surface significantly influence the thermal contact resistance, hence affecting the interface thermal transport.

Thus to improve through-thickness thermal conductivity in adhesive joints, the two driving factors are to minimize the impedance mismatch between the adhesive and the adherent interface as well as to minimize the interface contact resistance. There is an on-going effort by numerous researchers of dispersing conductive nano constituents (single wall carbon nanotube (SWCNT), multi wall carbon nano tube (MWCNT)) in polymers (adhesive) to enhance its thermal conductivity [1-3]. That improved the thermal conductivity of the nano modified adhesive only up to about of value of 0.6-0.7 W/mK. Their success in improving thermal conductivity was limited to due to nanotube ends terminating in the polymer causing phonon scattering at the naotube-polymer interface. To overcome the inherent thermal transport deficiency in polymer adhesive, in this paper aligned multi wall carbon Nanotubes (MWNT) are utilized in adhesives to enable through-thickness thermal transport in adhesive bonded joints. The processing scheme utilized of incorporating aligned MWNT and to minimize interface thermal contact resistance is discussed in the following sections.

2. Preliminary analysis of materials parameters for conductive adhesive joints

The materials configuration for processing the conductive adhesive joint is schematically shown below in Figure 1. We propose to use vertically aligned MWCNT in joints to enhance through-thickness conductivity [10] because of its known high thermal conductivity [11]. The MWCNT are selected to be infiltrated with adhesive between the adherent surfaces. The key parameters of improving through-thickness thermal conductivity, as discussed in the previous section, are to maintain thermal contact of the conducting phase (MWCNT in this case) and to minimize phonon scattering at the nanotube and adherent surface contact points.

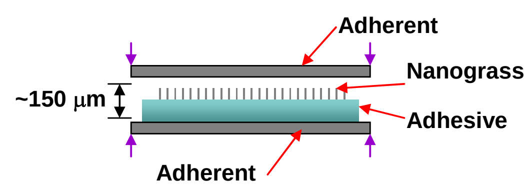

Figure 1. Schematic configuration of the Nanograss (MWCNT) with infiltrated adhesive in adhesive joint.

MWCNT films were grown on quartz substrates by chemical vapor deposition. The aligned CNT films were prepared by pyrolyzing iron (II) phthalocyanine under Ar/H_2 at 900°C as

described in details elsewhere [12]. The diameter of the tubes was 30 nm and the length of the MWCNT film was 30 μm. Figure 2 shows the cross-sectional view of the as produced MWCNT film. As evident for Figure 2, all nanotubes, as produced, are not perfectly aligned and also they are not of same height. Thus, as we process the adhesive bond, all the nanotubes are not expected to make contact with the adherent surface. Thus, a finite element analysis was performed to analyze the effect of MWCNT alignment, curvature and its end contact (interface) with the adhesive, etc.

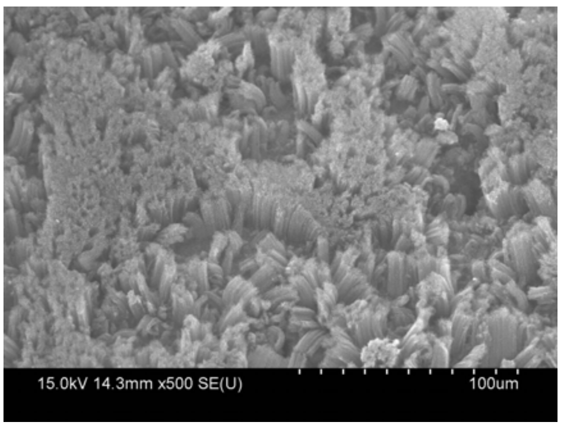

Figure 2. SEM image of the top view of as produced MWCNT film.

The geometric configuration of the finite element model (FEM) to analyze the effect of thermal conductivity of Nanotube, its curvature, and material thermal conductivity at the transition zone (location of the Nanotube-adhesive interface) is shown in Figure 3. It is determined in performing this FEM analysis that a transient heat transfer calculation is needed to be performed to analyze the effect of thermal conductivity of nanotubes. A representative result of analyzing the effect of Nanotube conductivity is shown in Figure 4.

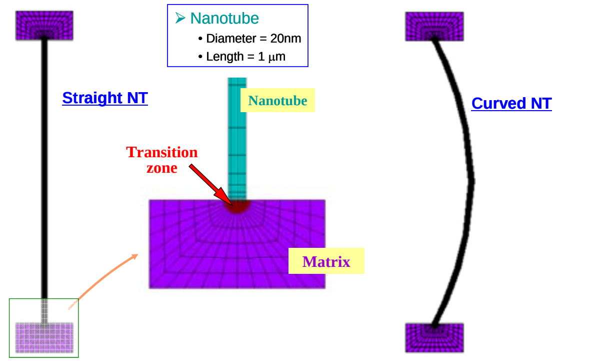

Figure 3. Geometric configuration of the finite element calculation.

As mentioned above, the effect of Nanotube curvature and conductivity of the transition zone is also analyzed. To summarize the FEM results, we found that the conductivity of the nanotubes and that of the transition zone strongly influence the through-thickness conductivity of the joint. The nanotube curvature hardly has any effect of the through-thickness conductivity, as long as the nanotubes possess adequate conductivity. In other words, from processing point of view, all nanotubes as processed need not be all aligned, as long as we have adequate number of nanotubes make thermal contact with the adherent surfaces. Also, special processing steps need to be made to ensure improving thermal conductivity of the transition zone to establish thermal contact and to minimize the impedance mismatch between the nanotubes and the adherents as well as adhesive. Based on the above findings, the processing steps incorporated in processing the adhesive joints are described in the next section.

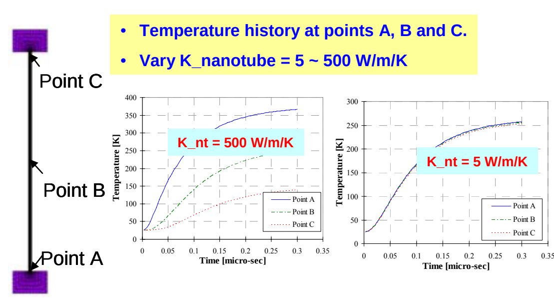

Figure 4. Transient heat transfer analysis of MWNT embedded in adhesive of varying conductivity.

3. Processing of aligned MWNT in adhesive joint

The aligned nanotubes were grown on a quartz substrate. The samples with the MWCNT side facing upwards were dipped in a beaker containing a 10% Epon 862/W - acetone solution. The film was then kept in a vacuum oven at 600°C for 2 hours for the solvent to escape. The epoxy was then cured at 177°C for 2 hours. The epoxy-MWCNT film was then peeled off the quartz substrate by etching with a 10% HF solution. The nanotube tips were exposed selectively by etching the film surface with 32 watt RF oxygen plasma for 30 minutes. The SEM images of the film after the plasma etching are shown in Figure 5. We observe from the figure that the nanotube tips are clipped due to the plasma etching. The side of the film which was previously anchored to the substrate was similarly etched in RF plasma under above mentioned conditions. Next, a 900 nm layer of gold was thermally evaporated on both sides of the film. Pyrolytic graphite face sheets were sputter coated with Au-Pd for 3 mins. After that a thin layer of Indium metal was melt coated on the substrates and the nanotube film. Finally the nanotube film was sandwiched between the graphite face sheets and fused together by heating at 175°C.

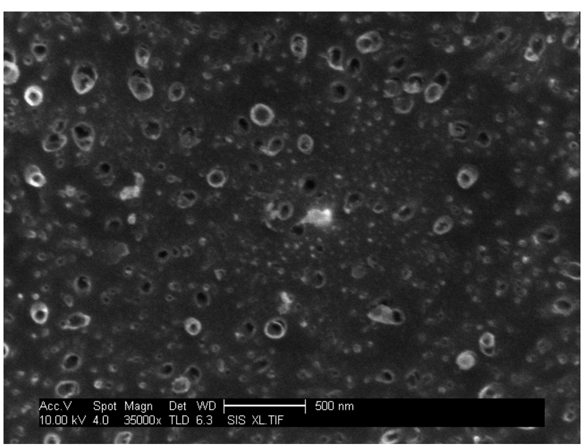

Figure 5. SEM image of the adhesive film with MWCNT tips exposed after the plasma etching.

4. Discussion of Results

Bulk thermal diffusivity measurements were measured using a Netzsch Laser flash apparatus under nitrogen purge. The laser flash technique allows measuring the thermal diffusivity (h) of solid materials over a temperature range -180°C to 2000°C. The laser flash (or heat pulse) technique consists of applying a short duration (< 1ms) heat pulse to one face of a parallel sided sample and monitoring the temperature rise on the opposite face as a function of time. This temperature rise is measured with an infrared detector. A laser is used to provide the heat pulse.

Heat capacity measurements were performed on a TA Instruments Q100 DSC. Based on the heat capacity and thermal diffusivity measurements measured the thermal conductivity for the device and a graphite reference was determined at 24°C. The thermal conductivity values for the graphite face sheet, the epoxy and the device were measured and are presented in Figure 6. The measured thermal conductivity for the graphite face sheet, the face sheets bonded by epoxy adhesive and the actual device was found to be 400, 3 and 262 W/mK respectively. Similar studies by Huang et al. [1] above showed considerably lower thermal conductivity of 1.21 W/mK. This was attributed to the phonon scattering at the interface. The better thermal conductivity achieved by our device may be attributed to the use of a metallic interface instead of a polymeric interface. The loss in thermal conductivity from the graphite face sheet is due to the use of Indium which has a thermal conductivity of ~ 70W/mK. Experiments are in progress using silver nanoparticles, which have a sintering temperature ~ 150°C. Further a new test method based on steady state heat flow is being devised to measure thermal conductivity at the nanoscale of bundles of tubes. This device is also envisioned to identify the loss in conductivity at the interface.

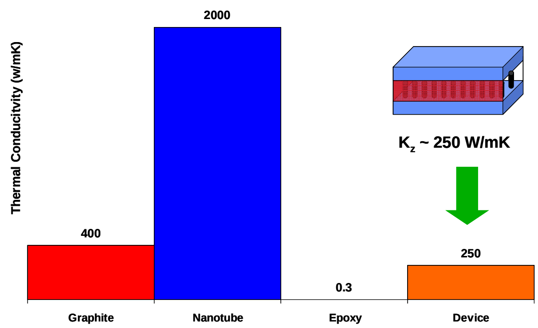

Figure 6. Measure through-thickness thermal conductivity of the adherent (face sheet), adhesive and the processed adhesive joint with vertically aligned MWCNT.

5. Summary

A concept of incorporating aligned conductive phase (MWCNT) in polymer adhesive joint is demonstrated to enhance through-thickness thermal conductivity in adhesive joints. It is observed that thermal contact of the conductive phase with the adherent surfaces needs to be established in order to achieve the desirable thermal transport through thickness. Further, acoustic impedance mismatch at the interface needs to be minimized to minimize the phone scattering to maximize thermal transport. The measured through-thickness thermal conductivity (K_z) of the joint configuration of aligned MWCNT infused with adhesive, using pyrolitic graphite face sheet was over 250 W/mK, which exceeds the through-thickness thermal conductivity requirement of adhesive joints for space structures by an order of magnitude. Since K_z of composite face sheets is much lower than that of pyrolitic graphite face sheets, the K_z of the same joint configuration using the composite face sheets is expected to be much lower than 250 W/mK.

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